

Confetti Ordering by Polymer Brushes

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Abstract

I consider the ordering of dilute platelet additives when incorporated into an end-grafted polymer brush. The competition between wetting interactions and the anisotropic stress environment of the interior of the brush causes these platelet additives to either remain suspended at the outer edge of the brush laying flat against the brush surface (as bits of confetti at rest on the ground), or to invade the interior of the brush in which case the platelets stand end-on and in some cases protrude above the outer edge of the brush. The orientation of the additives is controlled by the ratio of the diameter of the additive to the thickness of the bare brush, as well as the ratio of solvent-monomer and solvent-platelet interactions.

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I. INTRODUCTION

Self-assembly at the nanoscopic scale is responsible for an astonishing variety of materials properties in functional surfaces [1]. Homogeneously absorbed polymer layers are perhaps the simplest example, where the trapped polymer layer dramatically improves the ability of surfaces to avoid intimate contact (tribology)[2] or selectively absorb other target materials (cell-molecular lab-on-a-chip technology) [3]. At the cost of designing more complex surface-active materials, more interesting functionality and patterns can be engineered to self-assemble. Block copolymer thin films displaying an end-on “perpendicular” striped pattern, either through controlling competing wetting interactions [5], through employing asymmetric cylinder-forming diblocks[6], or through the application of external electric fields are all examples of patterned polymer films[7] that can be used to order a third, absorbed, material. Decorating these anisotropic patterns is a robust method for imparting a desired pattern to subsequent layers.

Central to ordering of the block copolymer layers is the subtle balance between the stretching of the chains, creating an anisotropic stress environment inside the brush, and substrate and solvent interactions between monomers favoring the copolymer domains to conform to the substrate. Many avenues of controlling the orientation and texture of the microsegregated patterns have been investigated [4, 8].

Long, thin, additives, however, can act locally as substrates themselves, so an interesting question is, what are the ordering boundary conditions on the hard surface of the additive? A grafted polymer layer is composed of anisotropic chains stretching away from the main substrate. Long thin additives can interact with a brush by adopting a configuration either interdigitating with the brush and standing end-on, or laying on top of the brush, as in confetti scattered on the ground. The additive will have to determine which orientation (and which penetration depth) is mechanically stable and the thermodynamic ground state orientation. Figure 1 has a schematic indicating the two possibilities.

The additives I consider here are impenetrable to the polymer brush monomers and are relatively flat. Additionally, I suppose a controllable interaction between the polymer brush and the solvent, and between the additive and the solvent. In a real physical system, this additive could be a graphene sheet [9], suitably decorated with side groups to control these interactions. Additionally, fully exfoliated inorganic clay sheets with typical dimensions

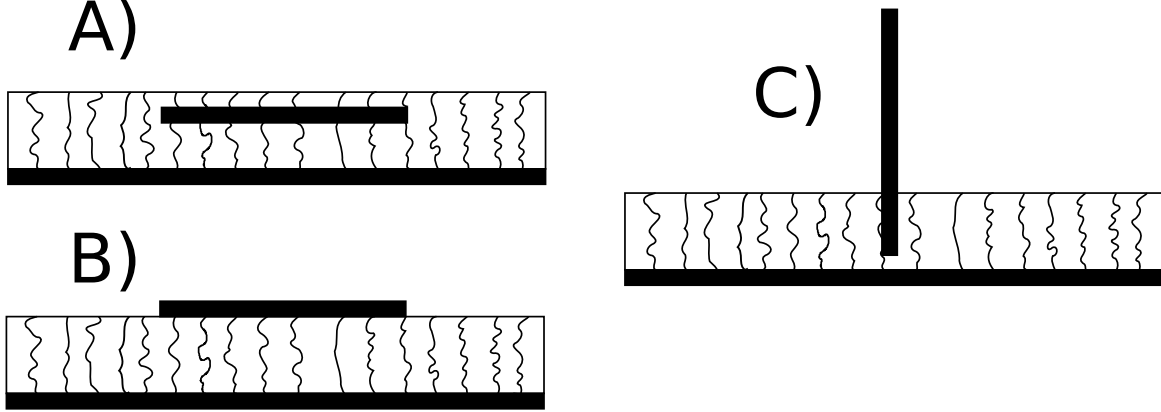


FIG. 1. A) The platelet additive is immersed and wetted with brush polymers, the *wetted* confetti configuration. B) The platelet additive rests on the surface of the brush, with an exposed dewetted surface, the *dewetted* confetti configuration. C) The platelet additive rests perpendicular to the brush.

on the scale of the brush heights could be employed to create a physically reasonable and technologically interesting instance of this scenario [11]. An even more interesting possibility is the ordering of carbon nanotubes (rather than graphene sheets) perpendicular to the film normal creating a smart surface that would switch from a forest of trunks extending from the surface to a “flattened forest” in which all the nanotubes lay along the surface. This possibility will be explored in subsequent work, as in Figure 1(C).

I will thus estimate the free energy penalty to insert an isotropic plate of typical dimension L into a polymer brush in each of the two orientations. This theory will make, necessarily, drastic assumptions simplifying the situation. The conclusions of this simple theory can be directly compared to a more computationally intensive Scheutjens’s and Fleer Self-Consistent-Field (SCF) lattice calculation [12]. Below, I exhibit the generalization to the two-dimensional lattice model [13] to encompass the presence of a freely-mobile, but interacting impenetrable plate. The most exciting result of this combined analytic and numerical approach is the identification of a significant region in the polymer-plate and polymer-solvent interaction space that results in the additives not only arranging themselves perpendicular to the brush, but also extending out past the *outer edge of the brush*. This regions is accessible through changing the solvent quality or the temperature, so there is the possibility that a “smart” surface, nominally made of organic material, will present an extreme roughness consisting of bare inorganic material plates, extending far above the

surface, ready to catch and hold several possible target materials.

II. SIMPLE MODEL

Consider a square, rigid plate of side length L that can interact first with an end-grafted polymer brush consisting of molecules with a degree of polymerization N , and a surface grafting density of σ chains per unit area. A small molecule solvent is present, with Flory-Huggins interaction parameters χ_p standing for the interaction between the *plate* and the solvent and χ_b standing for the interaction of the *brush* and the solvent. For this argument, I assume no energetic penalty or bonus for brush / plate contacts. Certainly, when $\chi_b = \chi_p$ there is no tendency for the platelet additive to either adsorb at the brush or invade it significantly. Increasing either χ_b or χ_p will trigger the absorption of the additive. On the one hand, the plate in an increasingly bad solvent environment will be able to shield its surface from bare contact with solvent by accumulating brush monomers at its surface. Alternatively, as the solvent quality becomes harsher and harsher for the brush, the plate will act as a compatibilizing agent, replacing some brush-solvent contacts with brush-plate contacts. The important question to address is how will the absorbed additive orient itself in the brush?

For well-soluble brushes ($0 < \chi_b < \Theta = 0.5$) and increasingly poor solvent conditions for the plate, the ultimate limit for the absorbed plate will have the absorbed plate completely wet with brush monomers. The plate itself will then act as a concentration center for an induced micelle of brush polymers, similar in structure to an “octopus” or “pinned micelle” [14, 15]. As in Figure 2, the length D_{pm} indicates the lateral extent of the brush grafting surface contributing chains to the structure, and is a function of brush grafting density, molecular weight, and brush solvent quality. Thus, we can estimate the free energy per plate for an initial “confetti” configuration in which both sides of the additive are wet with brush polymer:

$$F_{wet} = \sigma(L + D_{pm})^2(L + D_{pm})^2/N. \quad (1)$$

Here, the first term indicates number of chains involved in the structure, and the second term indicates the stretching energy per chain in the structure. As polymer-brush contacts are assumed to cost negligible free energy, and the plate is entirely sequestered from the solvent, there is no term for the surface energy of the plate. On the other hand, we can have

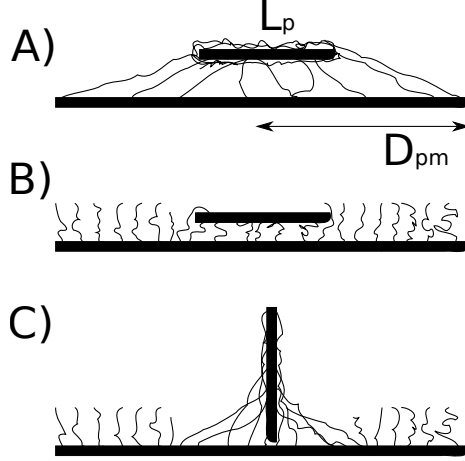


FIG. 2. A) The plate draws monomers from grafted chains extending as far as D_{pm} , and fully covers the plate. B) The solvent quality for the brush has worsened to the point that the plate dewets, exposing bare surface to solvent. C) Intermediate solvent qualities, the plate orients perpendicular to the surface.

a slightly lower stretching energy per chain, and fewer chains involved in the structure, in the perpendicular orientation:

$$F_{perp} = \sigma(L + D_{pm})L(L^2 + D_{pm}^2)/N, \quad (2)$$

indicating that there will be a transition from the “wetted confetti” configuration to the “perpendicular” orientation when

$$L \approx D_{pm}, \quad (3)$$

apart from an uninteresting factor of order unity. That is, when the plate itself is on the scale of the surface micelle its presence induces, the transition from the wetted confetti to the perpendicular orientation occurs.

The possibility exists that a further transition, from a perpendicular orientation to a detwetted confetti configuration, can occur when the plate has become so large that the enhanced stretching energy required for surface chains to extend all the way to the extreme tip of the plate is balanced by the reduction in stretching energy of a confetti orientation, with the outer surface of the plate wet with bad solvent, and bare of polymer. We can estimate the size of plate which causes such a transition. In this case, the stretching energy of individual chains in the perpendicular configuration are dominated by stretching over a

length scale L :

$$F_{str} = L^2/N \quad (4)$$

and the surface energy penalty for the bare exposed confetti surface is (near the transition in Eq. 3)

$$F_{surf} = \chi_p L^2 (L^2 \sigma)^{-1}. \quad (5)$$

The transition, should it occur, would require these energies to be on the same scale:

$$L^2/N = \chi_p L^2 (L^2 \sigma)^{-1} \rightarrow L^* = (N \chi_p / \sigma)^{1/2}. \quad (6)$$

If $L < L^*$, we can expect to increase χ_p without bound, and yet never induce the transition to the bare confetti structure, whereas, with $L > L^*$, there is the possibility that the perpendicular orientation is preempted by the dewetting of the upper surface of the confetti. The broad possibilities for a good-solvent brush are thus enumerated.

When the brush is poorly soluble, I expect all values of χ_p will result in the absorption of the plate. Now, we have a relatively straightforward comparison of surface energies in the three configurations. The wetted confetti configuration has a free energy cost of approximately

$$F_{wet} = (\sigma L a) L^2 / N + \chi_b L^2, \quad (7)$$

where the first term counts up all the chains grafted at the outer perimeter of the plate, and counts the cost for them to stretch across the upper surface of the plate. The second term counts the solvent-polymer surface energy. The perpendicular orientation, on the other hand, does not require stretching to coat both surfaces of the plate, and hence has a free energy cost of

$$F_{perp} = L^2 \chi_b, \quad (8)$$

as the brush-solvent contacts of the wetted configuration still occur for the perpendicular configuration. The expression for F_{perp} is correct up to the point where L exceeds the layer thickness of the grafted layer: $h = \sigma N$. When this occurs, there is the possibility that a bare edge of the plate protrudes past the edge of the brush, and we would then have to include the solvent-plate energy cost:

$$F_{perp} = L^2 \chi_b + (L - h) L \chi_p, \text{ when } L > h. \quad (9)$$

The detwetted confetti configuration will then have a free energy cost of

$$F_{confetti} = \chi_b L^2 \quad (10)$$

We thus expect that the wetted-confetti configuration to be stable from the good-solvent regime up to the bad solvent regime, where its stretching penalty destabilizes it to the perpendicular orientation. Under these circumstances, as long as $L < h$, that transitions from perpendicular to dewetted confetti occurs when

$$\chi_b > \chi_p. \quad (11)$$

Thus, increasing χ_b at fixed χ_p will eventually trigger a perpendicular-to-dewet transition. In this case, the flat-laying plates act as an anisotropic compatibilizer, getting between the polymer and solvent.

In a situation where $L > h$, the balance of energies between the two configurations implies a transition when

$$\chi_b L^2 + (L - h)L\chi_p = \chi_p L^2 \quad (12)$$

or when

$$\chi_b L \approx h\chi_p \quad (13)$$

thus stabilizing the wetted configuration when the exposed perpendicular segment of the plate has an area comparable to the whole plate area.

III. SELF-CONSISTENT FIELD RESULTS

I have executed Scheutjens-Fleer [12] calculations in a system in which I assume translational invariance in one direction. Thus, the plates I am formally considering are parallelepipeds with one small dimension (the lattice scale) one controllable dimension, L_p , and one very long direction aligned in the y -axis. The calculation lattice is $L_x = 60$ and $L_z = 30$ sites in dimensions for the calculations I present. In all that follows, I have kept the properties of the brush polymers fixed at $N = 150$ monomers, and $\sigma = 0.01$ grafted chains / surface lattice site. Thus, a fully-packed polymer layer would have a size of $N\sigma = 1.5$ extent in the z -direction. I consider additives with $L_p = 2, 4, 8$, and determine the equilibrium orientation of the additive by “holding” it a distance z_p above the grafting surface in each

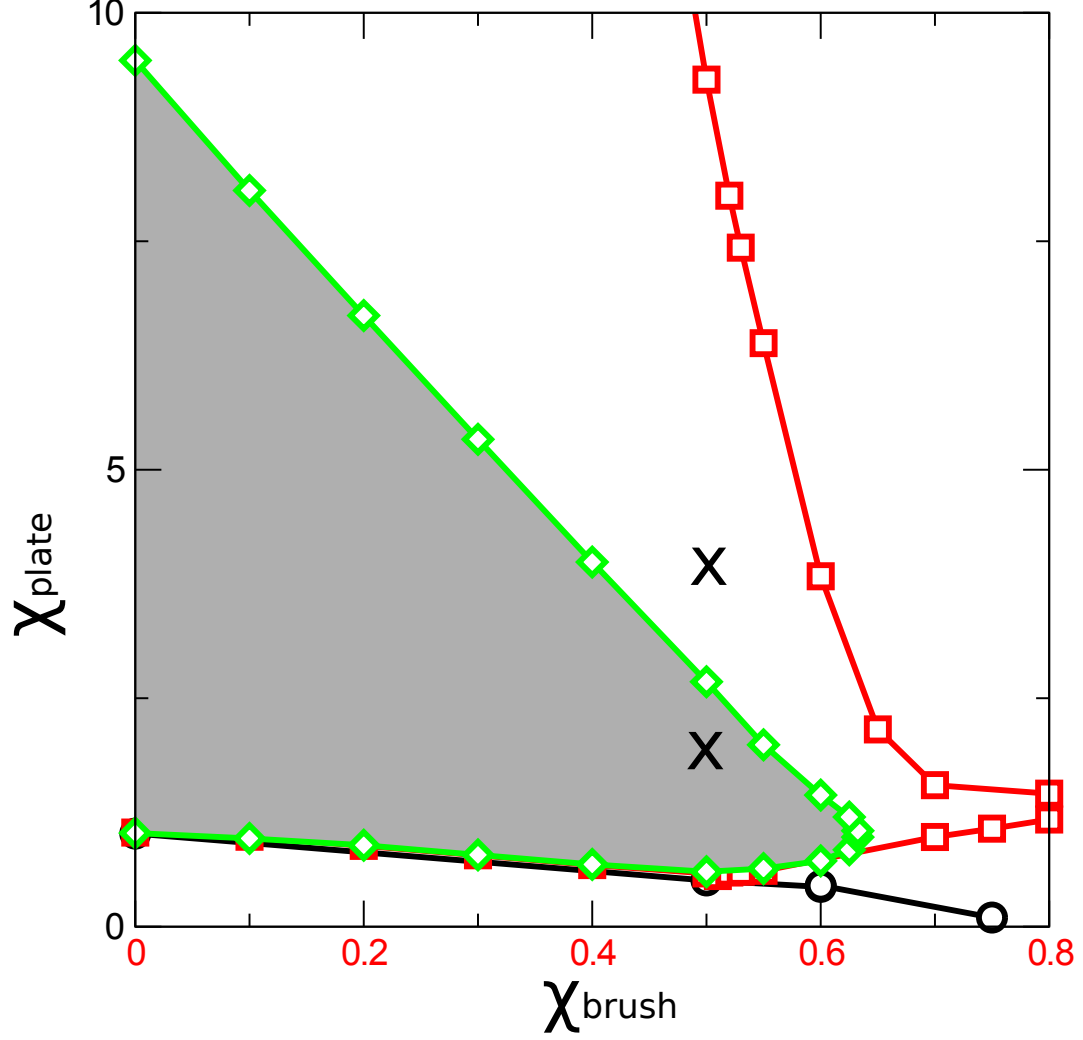


FIG. 3. When the plate is on the order of the fully compressed layer $L_z = 2$, black circles, the additives are “parallel” below the line, and “perpendicular” above it. For $L_p = 4$, there is a large region with perpendicular orientation (to the left and above the red square line). When the additive is much longer than the fully compressed polymer layer, $L_p = 8$, compared to a layer size of ≈ 2 , the region of perpendicular orientations is shaded on the diagram. Here, “reentrant” transitions from parallel-perpendicular-parallel occur generically. The two “X”’s mark parameters corresponding to the brush volume fraction profiles in Fig. 4.

orientation, and determining which z_p and corresponding orientation minimizes the overall system free energy for a single additive.

The additive is modeled as a region of L lattice sites completely filled with a volume

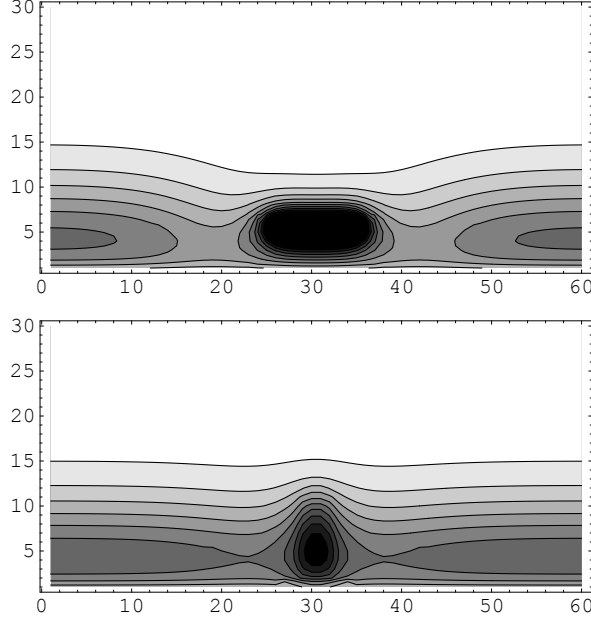


FIG. 4. The upper panel corresponds to $\chi_b = 0.5$ and $\chi_p = 4.0$ (the upper “X” in Fig. 3). The lower panel corresponds to $\chi_b = 0.5$ and $\chi_p = 2.0$ (the lower “X” in Fig. 3).

fraction of $\phi_p = 1$. There are two Flory-Huggins parameters in the problem. One, χ_b is the interaction parameter between the brush segments and the monomeric solvent. The other, χ_p is the plate-solvent interaction parameter. I have assumed that the interaction between polymer and plate has $\chi = 0$, as in the above. Thus, the solvent is the effective medium of interaction between the brush and the plate, modified by the connectivity of the polymer chains and the orientation of the additive.

Figure 3 shows the results of the calculation, showing the region where the perpendicular orientations exist. When $L_p = 2$, there is a small region of parallel orientations for both small χ_b and χ_p , but most of the parameter space is dominated by the perpendicular orientation. For plates a bit longer, $L = 4$, the scenario in the above section plays out. There are regions in which transitions from parallel-perpendicular-parallel occur (for increasing χ_b at $\chi_p = 0.6$, but when $\chi_b < 0.4$ even the unrealistically high value of $\chi_p = 10$ is insufficient to cause the additive to lay down. For much longer additives, $L_p = 8$, no matter what the plate-solvent interaction, there is always a point at which the polymer layer ejects the perpendicular plate, which then lays on top of the brush. In this scenario, the plate is wet with polymer.

IV. DISCUSSION

Several means of controlling surface properties of a polymer brush seem possible through this mechanism, and the collective orientation behavior for particles in the brush is worth of further study. At a minimum, *in situ* control of the brush layer as a surface in a many-step, hierarchical nanoscopic self-organization for device applications seems possible. With a change in solvent quality, the lateral area fraction of the brush covered by the additives can change discontinuously in going from the perpendicular to the dewetted parallel configuration. When many perpendicularly oriented additives are present, it is possible for the additives to behave as a two-dimensional confined “clay” material, with the possibility of liquid crystal phases in their lateral orientation, and perhaps a transition from a dilute “ex-foliated” structure to more densely packed configurations reminiscent of ceramic clays (albeit nanoscopically confined, end-on clays).

Also, I have made no attempt here to describe the dynamics of the additive when in the perpendicular configuration. It is possible that this configuration will change the effective dynamic boundary condition at the polymer surface, so that a shearing field for the solvent could have additive-controlled (and therefore switchable) transitions from stick to slip dynamic boundary conditions.

Even more interesting to me are the possibilities opened when the additives have a more complex geometry. Single-walled carbon nanotubes and nanowires are examples. A very interesting set of complex materials with exotic geometries can be constructed by designing DNA strands to form T-bars, tetrahedra, other complex shapes [16]. Such objects have the capability of not only orienting in multiple ways in the polymer layer, but of changing their conformations in response to the stress the grafted polymers put upon the additives.

V. CONCLUSION

Flat, hard additives added to an end-grafted polymer brush can orient either perpendicular or parallel to the polymer layer. The orientation is controlled by the ratio of the layer thickness and the size of the additive and the solvent interactions between the solvent and the brush and the solvent and the additive. An interesting perpendicular orientation in

which bare additive is exposed far from the surface occurs in intermediate solvent conditions.

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